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Microwave Spectrum, Structure, Quadrupole Interaction, Dipole Moment, and Bent C–Cl Bonds in 1,1dichlorocyclopropane

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observed under certain circumstances in liquid and gelatinous explosives.[28,29] The observed velocities are much lower than those predicted by the model of this paper, lying in the range 1–3 mm/μsec rather than the range 5–6.6 mm/μsec as predicted by Fig. 6. These low velocities are characteristic of heterogeneous or granular explosives which are generally acknowledged to react according to the grain-burning mechanism originally proposed by Eyring, Powell, Duffey, and Parlin.[4] The hypothesis that the low-velocity detonation waves in this instance are the result of reaction according to a grain-burning mechanism rather than according to thermal decomposition throughout a homogeneous medium is supported by the observation that these waves occur in aerated explosives, with the low velocity being favored when the bubbles are large.[28]

ACKNOWLEDGMENTS

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[28] Reference 20, Chap. 10.

[29] Reference 4, p. 135.

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Microwave Spectrum, Structure, Quadrupole Interaction, Dipole Moment, and Bent C—Cl Bonds in 1,1-dichlorocyclopropane*

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The microwave spectrum of $C_3H_4Cl_2^{35,35}$, $C_3H_4Cl_2^{35,37}$, $C_3D_4Cl_2^{35,35}$ $C_3D_4Cl_2^{35,37}$, $C_3H_3DCl_2^{35,35}$, $C_3H_3DCl_2^{35,37}$ (*cis* and *trans*), and $C_2C^{18}H_4Cl_2^{35,35}$ have been investigated. Using the derived rotational constants, a complete structure for the molecule is calculated. The structural parameters are $d_{\mathrm{C-H}}=1.085$ A, $d_{\mathrm{C(2)-C(3)}}=1.534$ A, $d_{\mathrm{C(1)-C(2)}}=1.532$ A, $d_{\mathrm{C-Cl}}=1.734$ A, $\angle \mathrm{H—C—H}=117°35'$, $\angle \mathrm{C(2)—C(3)—H_2}=153°37'\pm15'$, $\angle \mathrm{Cl—C—Cl}=114°38'$. κ for $C_2C^{13}H_4Cl_2^{35,35}$ was very close to zero (±0.0001), and it was not possible to determine its sign unambiguously. Using the negative value instead of the more likely positive value, a slightly different structure was obtained.

High-resolution measurements were carried out on the Cl nuclear quadrupole hyperfine structure in order to obtain the complete quadrupole coupling constant tensor in the $C_3H_4Cl_2^{35,35}$ principal inertial axis system. The values obtained are $\chi_{aa}=-43.545$ Mc, $\chi_{bb}=4.100$ Mc, $\chi_{cc}=39.445$ Mc, all ±0.005 and $\chi_{ab}=-51.5\pm0.3$ Mc. The principal quadrupole-coupling constant tensor elements are $\chi_{\alpha}=-76.4\pm0.3$ Mc, $\chi_{\beta}=37.0\pm0.3$ Mc, and $\chi_{cc}=39.445\pm0.005$ Mc. The angle between the principal quadrupole axis component along the C—Cl bond and the C—Cl internuclear line is $0\pm15'$. This is strong evidence against bent C—Cl bonds in this compound.

Detailed analysis of the Stark effect in the presence of quadrupole interaction leads to a dipole moment of 1.58 debye.

INTRODUCTION

In earlier work on methylene chloride,[1] it was found that both the HCH angle and the ClCCl angle were greater than tetrahedral, both angles being about 112°. From this it was inferred that the C—Cl bond was probably bent. In this earlier work, the quadrupole-coupling constants were also measured, but only the diagonal elements of the quadrupole-coupling tensors in the inertial axis system were determined since the first-order theory was adequate to explain all of the experimental data. As a result, it was not possible to find the orientation of the principal axes of the quadrupole tensors without making assumptions concerning the symmetry of the C—Cl bonds.

In the attempt to obtain more information concerning these or similar C—Cl bonds, the work on 1,1-dichlorocyclopropane was undertaken in the hopes of determining the direction of the principal axes of the chlorine nuclear quadrupole-coupling tensors. The axes of the quadrupole tensor represent the orientation of the electron cloud about the Cl atom. The angle between the C—Cl internuclear line and the axes of the quadrupole tensor should be a measure of the degree of bending in the carbon-chlorine bond.

The determination of the principal axes of the quadrupole-coupling constant tensors in 1,1-dichlorocyclopropane involves the determination of all the tensor elements in the principal inertial axis system. Using perturbation theory to calculate the energy, the off-diagonal elements enter only in the second order.

Unfortunately for our present purpose, first-order theory is wholly adequate to explain all of our spectral

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* Based in part on the doctoral theses of A. Narath (1959) and W. F. Flygare (1961) University of California, Berkeley.

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‡ Present address: Sandia Corporation, Albuquerque, New Mexico.

[1] R. J. Myers and W. D. Gwinn, J. Chem. Phys. **20**, 1420 (1952).

observations. Second-order effects would be large between two rotational levels of the proper symmetry, if they were nearly degenerate. All second-order interactions were calculated for rotational levels up to $J=12$, and none were found large enough for detection of the second-order effect.

An indirect method of determination of the orientation of the axis system was devised. The method consisted of a determination of the diagonal elements χ_{aa}, χ_{bb}, and χ_{cc} of the quadrupole-coupling constant tensors for Cl^{35} in $C_3H_4Cl^{35,35}$. The subscripts a, b, and c refer to the principal inertial axes. A second measurement of the coupling constants of Cl^{35} and Cl^{37} in the $C_3H_4Cl_2^{35,37}$ axis system, which is tilted relative to the previous system, enables an estimation of χ_{ab} and the determination of the orientation of the principal quadrupole-coupling constant tensor. This method required very high resolution and accuracy in the measurement of very weak lines.

EXPERIMENTAL

The basic spectrograph used in this work is essentially the same that has been used in this laboratory for many years. However, in order to work with 1,1-dichlorocyclopropane, it was necessary to make modifications. The complexity of quadrupole hyperfine structure placed a very high premium on resolution, while at the same time the weakness of the absorptions placed stringent demands upon sensitivity. There are available methods to obtain higher resolution than would ever be possible using a Stark modulated waveguide cell such as ours. The method giving by far the highest resolution is the maser, which was devised by Gordon *et. al.*[2] Video spectrographs are also capable of considerable improvement over Stark modulated spectrographs in resolution, but both video spectrographs and masers are limited to absorptions which are more intense than about 10^{-7}. Unfortunately, most lines in the spectrum of 1,1-dichlorocyclopropane are weaker than this.

High sensitivity with our present spectrograph requires long time constants and slow sweep rates of the frequency. The frequency instability of the klystron causes the resolution to decrease as the sweep rate is decreased, thus setting a lower limit to the sweep rate. To overcome this difficulty, a phase stable frequency stabilization system was developed with which the klystron was electronically locked to a stable, but variable, frequency standard.[3]

The frequency of the klystron is varied as slowly as desired by sweeping the variable-frequency oscillator, using a suitable clock motor. Markers are put on the record at convenient intervals by monitoring the variable frequency oscillator with a Hewlett-Packard frequency counter (524C).

A typical slow sweep enables one to use a time constant as long as one minute and to place markers every 5 or 10 kc on the record. Using low pressures to decrease linewidth, frequency measurements can be made to an accuracy of 5 or 10 kc.

Since Stark components seriously interfered with the observation of the quadrupole fine structure, the exponential-type modulation[1] (also see asterisk reference) was used to essentially eliminate the Stark components from the recorded spectrum. To increase the population of the lower levels, all high resolution studies were made with the waveguide chilled to dry ice temperatures. A comparison of the resolution obtained by our conventional spectrograph with that obtained by the stabilized system is shown later in the section on Quadrupole Interaction [Figs. 3(a), (b), and (c)].

The normal species $C_3H_4Cl_2$ was obtained from Columbia Organic Chemicals Company, Incorporated, and was purified by fractional distillation.

The isotopic species were prepared as follows:

$C_3D_4Cl_2$. Malonic ester was reduced by $LiAlD_4$ to give $HOCD_2CH_2CD_2OH$, which was refluxed with a HBr (48%) solution and H_2SO_4 to give the trimethylene bromide derivative $BrCD_2CH_2CD_2Br$. The ring was closed by the reaction between $BrCD_2CH_2CD_2Br$ and zinc dust in an alcohol solution giving $C_3H_2D_4$. Gaseous $C_3H_2D_4$ and Cl_2 were photolyzed using a 100-w tungsten bulb. As a result of a large isotope effect, the sample was almost entirely $C_3D_4Cl_2$. The sample of $C_3D_4Cl_2$ was purified by vaporphase chromatography.

$C_3H_3DCl_2$. The $BrCH_2CH_2CHDBr$ synthesis followed that of Kharasch and Mayo.[4] The rest of the synthesis was the same as above.

SPECTRUM AND ASSIGNMENTS

Approximate rotational constants were calculated using values obtained from electron diffraction studies[5] and using reasonable hydrogen parameters. From the approximate moments of inertia it was calculated that the rotational energy levels up to $J=70$ would be appreciably populated even at dry-ice temperatures. Lower temperatures could not be used due to vapor pressure limitations. The spectrum is, therefore, very dense, averaging about a multiplet every 25 Mc in the 8–15 kMc region, and it is much denser at the higher frequencies.

Several attempts to make an assignment in the 24 kMc region on consistency of rotational constants alone failed. Identification of a transition by its Stark components could not be applied due to the large quadrupole perturbation. It became apparent that the only

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[2] S. P. Gordon, H. J. Zieger, and C. H. Townes, Phys. Rev. **95**, 282 (1954); **99**, 1264 (1955).

[3] A. Narath and W. D. Gwinn, Rev. Sci. Instr. (to be published) (see also A. Narath, Ph.D. thesis, University of California, Berkeley, 1959).

[4] M. S. Kharasch and F. R. Mayo, J. Am. Chem. Soc. **55**, 2468 (1933).

[5] J. M. O'Gorman and V. Schomaker, J. Am. Chem. Soc. **68**, 1138 (1946).

TABLE I. Assigned transitions for the isotopic species studied in 1,1-dichlorocyclopropane.

	$C_3H_4Cl_2^{35}$	$C_3H_4Cl_2^{35,37}$	$C_3D_4Cl_2^{35}$	$C_3D_4Cl_2^{35,37}$	$C_3H_3DCl_2^{35}$	$C_3H_3DCl_2^{35,37}$ (*cis*)	$C_3H_3DCl^{35,37}$ (*trans*)	$C_2C^{13}H_4Cl_2^{35}$ ($\kappa=+0.0001$)
4_{04}–4_{13}	8955.2				8767.0			
4_{14}–4_{23}	9967.5	9861.9	8605.0					
4_{23}–4_{32}	8909.3							
4_{31}–4_{40}	9598.3	9899.9					8995.9	
4_{32}–4_{41}		10 580.7						
5_{05}–5_{14}					11 772.1	11 529.8		
5_{24}–5_{33}	10 441.2							
5_{32}–5_{41}		8857.4						
5_{33}–5_{42}	10 694.4	10 863.7			9964.8			
5_{41}–5_{50}			8958.4		11 752.0			
5_{42}–5_{51}			9448.0	9743.7				
6_{15}–6_{24}	11 007.3							
6_{34}–6_{43}	11 521.0	11 601.2	9242.3	9275.7	10 863.8	10 957.8	10 903.5	
6_{42}–6_{51}						11 361.1	11 206.5	
6_{43}–6_{52}			9554.8	9806.0				
7_{25}–7_{34}	9489.9		9425.7	9064.3	9488.8		9141.0	
7_{43}–7_{52}	10 603.1	11 121.9						
8_{35}–8_{44}	9447.6	8259.2	8297.0					8487.4
8_{44}–8_{53}	9252.1						8625.4	8485.0
8_{53}–8_{62}			9075.4	9689.8				
9_{36}–9_{45}					11 236.2	10 652.8	10 758.8	
9_{45}–9_{54}	8836.8	9025.6						
9_{46}–9_{55}								14 958
9_{55}–9_{64}								14 958
10_{46}–10_{55}				9560.8		9516.9		10 060.25
10_{55}–10_{64}						10 455.2	10 270.1	10 058.20
11_{47}–11_{56}								13 171
11_{65}–11_{74}								13 171
1_{01}–2_{12}	9833.3			8831.3	9592.8			
1_{11}–2_{02}	8250.4				8191.0			
1_{10}–2_{21}	13 899.3	13 781.8		12 096.5	13 429.5			
2_{02}–3_{13}	13 447.3	13 232.1	12 403.3	12 202.5				
2_{11}–3_{22}			15 869.4					
2_{12}–3_{03}			12 062.6		12 569.5			
3_{03}–4_{14}		16 826.1		15 665.6				
3_{12}–4_{23}								20 853.91
3_{13}–4_{04}			15 860.2					
4_{04}–5_{51}								20 728.54

solution to the spectrum would come from identification of low J lines by the quadrupole splittings. Toward this end the frequency stabilization system was designed. The region from 8–12 kMc was thoroughly searched, and several triplets were observed, presumably Q-branch transitions of J less than about eight, as well as other multiplets. Using the coupling constants of methylene chloride, approximate multiplet patterns

TABLE II. Rotational parameters in kMc and derived moments of inertia in amu A².

Species	$C_3H_4Cl_2^{35}$	$C_3H_4Cl_2^{35,37}$	$C_3D_4Cl_2^{35}$	$C_3D_4Cl_2^{35,37}$	$C_3H_3DCl_2^{35}$	$D_3H_3DCl_2^{35,37}$ (*cis*)	$C_3H_3DCl_2^{35,37}$ (*trans*)	$C_2C^{13}H_4Cl_2^{35}$ ($\kappa=+0.0001$)
$A-C/2$	1.01654	1.02213	0.81076	0.81634	0.95919	0.96694	0.96237	0.97895[a]
$A+C/2$	2.96655	2.93440	2.64491	2.61595	2.87776			2.91045[a]
κ	−0.04570	−0.08250	0.14407	0.10085	0.00133	−0.04213	−0.03178	0.0001[a]
I_a	126.9207	127.7731	146.2923	147.2888	131.7552			129.978[a]
I_b	173.1235	177.3774	183.0525	187.3556	175.5925			173.692[a]
I_c	259.2476	264.3654	275.6252	280.9153	263.4973			261.733[a]

[a] If κ is taken as −0.0001, then $a-c/2=0.97889$ and $a+c/2=2.910\,42$, with corresponding changes in I_a, I_b, and I_c.

were calculated. Several low J multiplets were then resolved using the new high-resolution system. By comparison of the experimental multiplet with calculated patterns, a Q-branch assignment was soon obtained. Next the quadrupole-coupling constants were accurately determined. From these data the approximate frequencies of several R-branch transitions were calculated. These were found and identified by their quadrupole-hyperfine structure.

The spectra of $C_3H_4Cl^{35}Cl^{37}$, $C_3D_4Cl^{35}Cl^{35}$, $C_3D_4Cl^{35}Cl^{37}$, and $C_3H_3DCl^{35}Cl^{35}$ were interpreted using similar methods. The isotopic species $C_3H_3DCl^{35}Cl^{37}$ (*cis* and *trans*) were also studied, but an assignment was obtained only for the Q-branch transitions, since the R-branch lines were all obscured by strong lines from other isotopic species.

The spectrum of $C_2C^{13}H_4Cl_2^{35}$ [natural abundance of C^{13} on the C(2) or C(3) position] was assigned on the basis of consistency alone. No quantitative quadrupole-splitting measurements could be made. The value of κ was obtained from the splitting of the 8–8 and 10–10 lines. The sign of κ cannot be obtained from these measurements. Using the value of κ obtained from the Q-branch lines, the remaining parameters $\frac{1}{2}(A-C)$ and $\frac{1}{2}(A+C)$ were obtained from the two R-branch lines. Calculations will be carried out using both signs of κ.

The assignments are listed in Table I, and the derived rotational parameters are listed in Table II.

STRUCTURE

The axis system used for the structural calculations is shown in Fig. 1. The x direction is taken along the C_{2v} symmetry axis. The z direction is taken out of the molecular plane. The origin of the coordinate system is taken at the center of mass of the normal isotopic species.

The moments of inertia of the unsymmetric species were transformed to this axis system. In some of the more unsymmetrical isotopic species, a three-dimensional rotation was required. The rotation was taken as the inverse transformation which diagonalized the inertial tensor as calculated from a trial structure and the coordinate system of Fig. 1. On the completion of the structural determination, second approximations for all these rotations were made. In all cases, they were found to be well within the limits of error of the first approximation. The effective moments of inertia were then combined to yield sets of equations of the type:

$$(I_{xx}+I_{zz}-I_{yy})+\Delta_y=2\sum_i m_i y_i^2-My_{cg}^2. \qquad (1)$$

The y_{cg} is the y coordinate of the center of mass. The inertial defect Δ_y is a result of the vibration-rotation interaction. Costain[6] has shown that good approximations to the equilibrium coordinates may be obtained by assuming Δ_x, Δ_y, and Δ_z to be independent of isotopic substitution. In this method, two equations are formed by substituting data from two isotopic species into Eq. (1). By subtracting the two equations, the inertial defect cancels and one obtains the substitution coordinates.

z coordinates. Both z coordinates may be calculated as substitution coordinates. Doing this, we obtain $z_H^2=0.862\pm0.001$ from $C_3H_4Cl_2^{35}$ and $C_3D_4Cl_2^{35}$ and $z_H^2=0.867\pm0.001$ from $C_3H_4Cl_2^{35}$ and $C_3H_3DCl_2^{35}$. Likewise, $z_{Cl}^2=2.131\pm0.001$ from $C_3H_4Cl_2^{35}$ and $C_3H_4Cl_2^{35,37}$

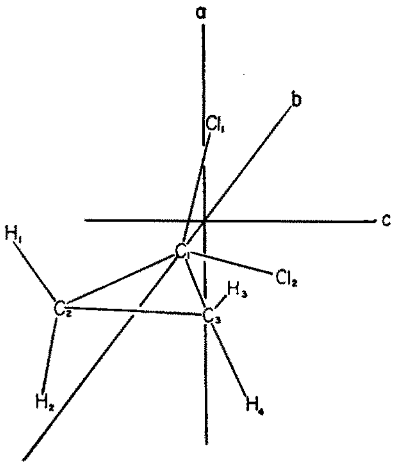

FIG. 1. 1,1-dichlorocyclopropane.

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[6] C. C. Costain, J. Chem. Phys. **29**, 864 (1958).

TABLE III. Comparison of various parameters for $\kappa=\pm0.001$ in $C_2C^{13}H_4Cl_2^{35}$.

κ	y_C	$d_{C(2)-C(3)}$	$(I_x+I_y-I_z)_a - (I_x+I_y-I_z)_b$
+0.0001	0.7670 A	1.534 A	0.004
−0.0001	0.7711 A	1.542 A	0.031

[a] $C_2C^{13}H_4Cl_2^{35}$.
[b] $C_3H_4Cl_2^{35}$.

and 2.132±0.001 from $C_3D_4Cl_2^{35}$ and $C_3D_4Cl_2^{35,37}$. The average values obtained are $z_H=0.929\pm0.002$ A and $z_{Cl}=1.460\pm0.001$ A.

In older methods, Δ is often neglected. If this is done by using Eq. (1) and plotting z_{Cl}^2 vs z_H^2, $z_H=0.928\pm0.002$ A and $z_{Cl}=1.460\pm0.001$ A are obtained. It is apparent that the inertial defect out of the plane of the cyclopropane ring Δ_z, is very likely small, and these coordinates are relatively insensitive to uncertainties arising from vibration-rotation interaction.

y coordinates. By direct substitution, one obtains from $C_3H_4Cl_2^{35}$, $C_3D_4Cl_2^{35}$, and $C_3H_4Cl_2^{35,37}$, $C_3D_4Cl_2^{35,37}$, $y_H^2=1.605\pm0.001$ and 1.607 ± 0.001, respectively, yielding an average of $y_H=1.267\pm0.001$ A.

y_C can be obtained from the $C_3H_4Cl_2^{35}$, $C_2C^{13}H_4Cl_2^{35}$ couple and Eq. (1). However, the value obtained will be independent on the undetermined sign of κ in $C_2C^{13}H_4Cl_2^{35}$. Distances were calculated using both signs of κ, and these are given in Table III.

In the last column of Table III, the differences in $\sum m_i z_i^2+\Delta_z$ for the normal and for the C^{13} isotopic species are tabulated for the two possibilities. This difference should be zero. Using $\kappa=+0.0001$, this difference is essentially zero (0.004±0.003); however, using $\kappa=-0.0001$, it is 0.031±0.003 which seems excessive. Unfortunately, this is not large enough to eliminate completely the possibility that $\kappa=-0.0001$, but it does give a strong indication that +0.0001 is the correct value. The structure will be found using both values, but considerable preference will be given to the structure calculated using $\kappa=+0.0001$. Since κ is so close to zero, little difference will be found between these structures.

Using Eq. (1), and plotting y_C^2 vs y_H^2 for all isotopic species except $C_2C^{13}H_4Cl_2^{35}$, one obtains values of $y_C=0.761\pm0.001$ A and $y_H=1.267\pm0.001$ A. From this, one notes that the inertial defect remains unimportant for a determination of y_H, but is evident in the determination of y_C.

x coordinates. Using the $C_3H_4Cl_2^{35}$, $C_3H_4Cl_2^{35,37}$ couple, one obtains $x_{Cl}=.6883\pm0.0002$. Using the $C_3H_4Cl_2^{35}$, $C_3H_3DCl_2^{35}$ and $C_3H_4Cl_2^{35}$, $C_3D_4Cl_2^{35}$ equations one obtains an average value of $x_H=1.8230\pm0.0002$. Using the $C_3H_4Cl_2^{35}$, $C_2C^{13}H_4Cl_2$ couple, one obtains $x_{C_{2,3}}=1.575\pm0.001$ A (if κ were −0.0001, this value would be 1.573±0.001 A). The remaining x_{C_1} parameter can be obtained from the first moment equation $0=\sum_i m_i x_i$. The value obtained is $x_{C_1}=-0.249\pm.001$ (−0.253 for $\kappa=-0.0001$).

Using these and the y, z parameter, a complete structure can be calculated. The results are in Table IV. It is seen from the results that κ positive gives the most likely structure for the molecule.

QUADRUPOLE INTERACTION

The fine structure in the rotational transitions is caused by the interaction of the nuclear quadrupole moments of the Cl nuclei with the electric field gradients at these nuclei. In most cases, this interaction is small, and perturbation theory can be used to obtain resultant energy levels. The matrix elements of the perturbation operator, in the case of equivalent or near equivalent nuclei, are most easily written in the $I_1I_2IJFM_F$ representation as described elsewhere.[1,7] The matrix elements simplify to the following form:

$$\left.\begin{aligned}&\langle I_1I_2I'J'FM_F\,|\,H_{Q_1}+H_{Q_2}\,|\,I_1I_2IJFM_F\rangle\\&\quad=f(I_1I_2I'J'F)\\&\quad\times[eQ_1\langle\partial^2V/\partial z^2\rangle_1+(-1)^{I'-I}eQ_2\langle\partial^2V/\partial z^2\rangle_2]\\&\quad=f(I_1I_2I'J'F)\chi^+\quad\text{if}\quad I-I'=0,\pm2\\&\quad=f(I_1I_2I'J'F)\chi^-\quad\text{if}\quad I-I'=\pm1\end{aligned}\right\}. \qquad (2)$$

H_{Q_1} and H_{Q_2} are the perturbation operators for the respective nuclei. Q_1 and Q_2 are the quadrupole moments of the nuclei, and $\langle\partial^2V/\partial z^2\rangle_1$, $\langle\partial^2V/\partial z^2\rangle_2$ are the electric field gradients at the respective nuclei. These are related to the components of the field gradient tensor in the principal inertial axis system by the direction cosines as shown by Bragg.[8] The expansion is as follows:

$$eQ\langle\partial^2V/\partial z^2\rangle=\langle\alpha_{za}\rangle^2\chi_{aa}+\langle\alpha_{zb}\rangle^2\chi_{bb}+\langle\alpha_{zc}\rangle^2\chi_{cc}$$
$$+2\langle\alpha_{za}\alpha_{zb}\rangle\chi_{ab}+2\langle\alpha_{za}\alpha_{zc}\rangle\chi_{ac}+2\langle\alpha_{zb}\alpha_{zc}\rangle\chi_{bc}, \qquad (3)$$

TABLE IV. Values of the structural parameters for $\kappa\pm$ in $C_2C^{13}H_4Cl_2^{35}$

	$\kappa=0.0001$	$\kappa=-0.0001$
∠H—C—H	117°35′±30′	117°35′±30
d_{C-H}	1.085±0.002 A	1.085±0.002 A
$d_{C(2)-C(3)}$	1.534±0.004	1.542±0.004
∠C(2)−C(3)—H_2	153°37′±15′	153°18′±15′
$d_{C(1)-C(2)}$	1.532±0.004	1.529±0.004
d_{C-Cl}	1.734±0.002	1.737±0.002
∠Cl—C—Cl	114°38′±15′	114°24′±15′

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[7] G. W. Robinson and C. D. Cornwell, J. Chem. Phys. **21**, 1436 (1953).
[8] J. K. Bragg, Phys. Rev. **74**, 533 (1948).

where $\langle\alpha_{ga}\rangle$ are the direction cosine matrix elements in the representation in which the rotational Hamiltonian is diagonal, and $\chi_{aa}=\langle\partial^2V/\partial a^2\rangle eQ$, etc.

In 1-1,dichlorocyclopropane $\langle\partial^2V/\partial a\partial c\rangle$ and $\langle\partial^2V/\partial b\partial c\rangle$ are zero by symmetry. The matrix elements $\langle\alpha_{za}\alpha_{zb}\rangle$ are off diagonal in J, and thus χ_{ab} enters only in second-order perturbation theory. All of our calculations will be carried only to the first order, using the methods of Bragg and Golden.[9]

In the case of identical coupling,[1] the assignment of phase in the intensity matrix is arbitrary. However, in the calculation of relative intensities considerable care must be exercised in assigning phases when the coupling is nonidentical. Nuclear spin statistics must also be taken into account when computing the relative intensities of the multiplets.

Several transitions were studied in $C_3H_4Cl_2^{35}$ and $C_3D_4Cl_2^{35}$ under very high resolution using the klystron stabilization system. Since $\chi_{aa}+\chi_{bb}+\chi_{cc}=0$, measurement of the quadrupole-fine structure of two transitions is all that is necessary to obtain the diagonal quadrupole-coupling constants. In this case several transitions were studied and the results plotted as χ_{aa} vs χ_{cc} for each transition. The intersection gives the correct values of the coupling constants. The consistency of these measurements for $C_3H_4Cl_2^{35}$ is shown in Fig. 2 and enables us to assign an uncertainty of ±0.005 Mc in χ_{aa} and χ_{cc}. The values of the coupling constants for Cl^{35} in $C_3H_4Cl_2^{35}$ and $C_3D_4Cl_2^{35}$ are found in Table V.

As stated earlier, χ_{ab} could be directly measured if a suitable near degeneracy were found. A large direction cosine, $\langle\alpha_{za}\alpha_{zb}\rangle$, must be found which connects near degenerate levels. The interactions are limited to $A\leftrightarrow B_c$ and $B_a\leftrightarrow B_b$ levels. Up to $J=12$ no such degeneracies were found.

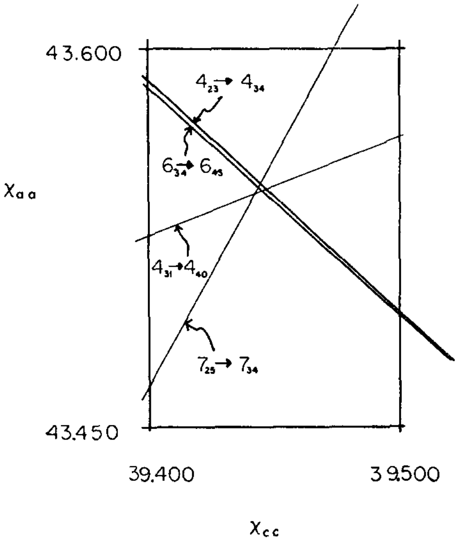

FIG. 2. χ_{aa} vs χ_{cc} for several rotational transitions of $C_3H_4Cl_2^{35}$. The values for the coupling constants are found in Table V.

TABLE V. Quadrupole coupling constants for Cl^{35} in the $C_3H_4Cl_2^{35}$ principal inertial axis system.

	$C_3H_4Cl_2^{35}$	$C_3D_4Cl_2^{35}$
χ_{aa}	−43.545±0.005 Mc	−43.45±0.05 Mc
χ_{bb}	4.100±0.010 Mc	3.96±0.10 Mc
χ_{cc}	39.445±0.005 Mc	39.49±0.05 Mc

The other way of obtaining χ_{ab} is by measuring the quadrupole interactions in two different principal inertial axis systems. Consider the following:

$$\begin{pmatrix}\chi_{aa} & \chi_{ab} & 0\\ \chi_{ba} & \chi_{bb} & 0\\ 0 & 0 & \chi_{cc}\end{pmatrix}=T^{-1}\begin{pmatrix}\chi_{\alpha} & 0 & 0\\ 0 & \chi_{\beta} & 0\\ 0 & 0 & \chi_{\gamma}\end{pmatrix}T, \tag{4}$$

where a, b, and c refer to the principal inertial axis system of $C_3H_4Cl_2^{35}$ and α, β, and γ refer to the principal quadrupole-coupling constant axes system.

$$T=\begin{pmatrix}\cos\theta & \sin\theta & 0\\ -\sin\theta & \cos\theta & 0\\ 0 & 0 & 1\end{pmatrix} \tag{5}$$

where θ = angle between the a axis and the α axis. By manipulation of Eqs. (4) and (5) we get

$$\chi_{\alpha}=\frac{\chi_{aa}\cos^2\theta-\chi_{bb}\sin^2\theta}{\cos^2\theta-\sin^2\theta}$$

$$\chi_{\beta}=\frac{\chi_{bb}\cos\theta^2-\chi_{aa}\sin^2\theta}{\cos^2\theta-\sin^2\theta} \tag{6}$$

$$\chi_{\gamma}=\chi_{cc}.$$

If we now substitute a Cl^{37} for one of the Cl^{35} nuclei, the new principal inertial axis system will have a slightly different orientation with respect to the principal axis systems of the quadrupole coupling tensors. As a result, the diagonal elements of χ in the new axis system are given by

$$\begin{aligned}
Cl_1^{35}\quad &\chi_{a'a'}=\chi_{\alpha}\cos^2(\theta+\phi)+\chi_{\beta}\sin^2(\theta+\phi)\\
&\chi_{b'b'}=\chi_{\alpha}\sin^2(\theta+\phi)+\chi_{\beta}\cos^2(\theta+\phi)\\
&\chi_{c'c'}=\chi_{\gamma}=\chi_{cc}\\
Cl_2^{37}\quad &\chi_{a'a'}=[\chi_{\alpha}\cos^2(\theta-\phi)+\chi_{\beta}\sin^2(\theta-\phi)]0.78802 \qquad (7)\\
&\chi_{b'b'}=[\chi_{\alpha}\sin^2(\theta-\phi)+\chi_{\beta}\cos^2(\theta-\phi)]0.78802\\
&\chi_{c'c'}=[\chi_{cc}]0.78802,
\end{aligned}$$

where a', b', and c' refer to the principal inertial axis system of $C_3H_4Cl_2^{35,37}$. The value 0.78802 is the ratio

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[9] J. K. Bragg and S. Golden, Phys. Rev. **75**, 735 (1949).

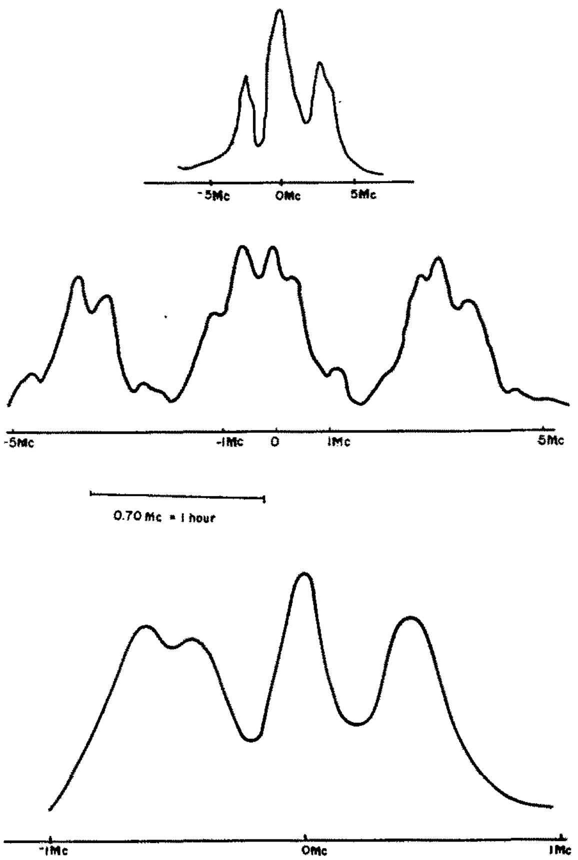

FIG. 3. The three parts give the sequence followed in resolving a multiplet. (a) is the $7_{43}\rightarrow 7_{52}$ transition of $C_3H_4Cl_2^{35,37}$ as traced from the record roll of our conventional spectrograph. (b) is the same line swept with the phase stabilization system. (c) is the center of the multiplet under very slow sweep conditions.

of Q^{37}/Q^{35} as given by Geschwind *et al.*[10] ϕ is the angle between the $C_3H_4Cl_2^{35}$ and $C_3H_4Cl_2^{35,37}$ principal inertial axis systems which is 2°17′.

Substituting (6) into (7) we obtain the coupling constants of Cl^{35} and Cl^{37} in the $C_3H_4Cl_2^{35,37}$ principal inertial axis system expressed as a function of one unknown parameter θ. Substituting (7) into (3) for each nucleus, one can evaluate χ^+ and χ^- in Eq. (2). Consequently, the energy splittings, as described by (2), are expressed as a function of θ.

Since the variation of χ_1 with θ is almost compensated by an opposite variation in χ_2, χ^+ is approximately independent of θ. It was therefore necessary to find a transition whose fine structure showed a strong dependence on χ^-. Values of χ^+ and χ^- were calculated for all assigned transitions of $C_3H_4Cl_2^{35,37}$, and the $7_{43}-7_{52}$ line exhibited the strongest dependence on θ. Energy levels for this transition were calculated for several possible values of θ.

To calculate relative intensities, the arbitrary phase assignment was obviated by writing both the Hamiltonian and intensity matrix using Racah[11] coefficients. The Hamiltonian was then transformed to the diagonal form and the same transformation was applied to calculate the intensities. These calculations were carried out on the IBM 704 digital computer.

In analyzing the results of the calculations, it is seen that the components most dependent upon θ lie near the center of the line, the outside wings being nearly independent of θ. Several of the center components move approximately 0.2 Mc with a change of one degree in θ. Thus we have a fairly sensitive measurement of θ.

To resolve the multiplet, the phase-sensitive klystron-stabilization system was used. The results compared with the unstabilized klystron are shown in Fig. 3(a), (b), and (c). To obtain the center of the multiplet [Fig. 3(c)], very long time constants (1 min) were used with very slow sweep rates (0.7 Mc/hr). Complete resolution was not obtained, however, as the trace in Fig. 3(c) is composed of many line components. To obtain the actual energy splittings and subsequently

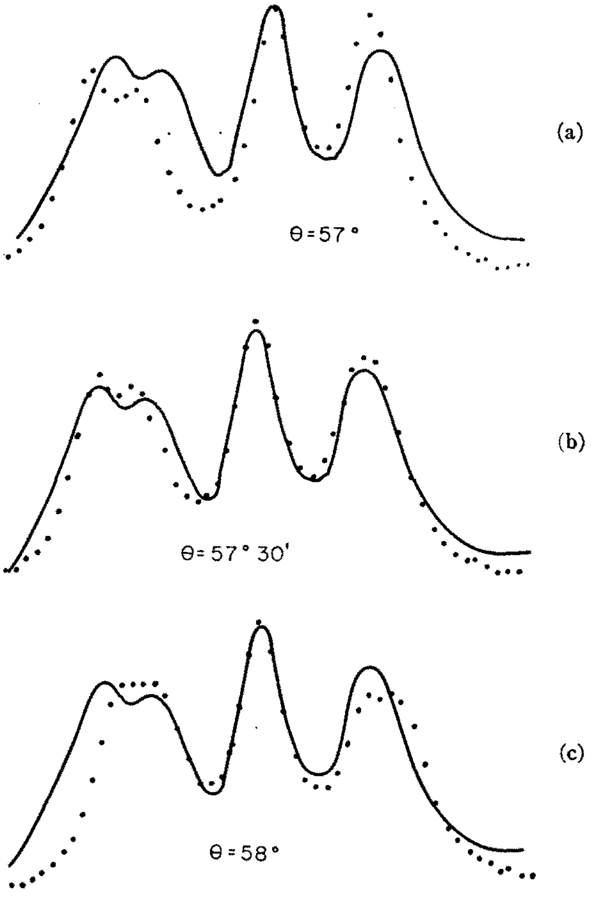

FIG. 4. These figures give a comparison of the line synthesis calculations with the recorder trace of the center of the multiplet as shown in Fig. 3 (c). The dots are the 704 computer printout which is normalized to the recorder trace of the multiplet. The line synthesis calculations were done for the three angles shown.

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[10] S. Geschwind, R. Gunther-Mohr, and C. H. Townes, Phys. Rev. **81**, 288L (1951); **82**, 344A (1951).

[11] G. Racah, Phys. Rev. **62**, 438 (1942).

θ from the apparent splittings in Fig. 3(c), line synthesis calculations were necessary. These calculations were carried out on the 704 computer. The input data consisted of the multiplet components and their relative intensities as calculated above and the experimental linewidths. Using a Lorentz-type function for the line shapes, the band contours were calculated and plotted out on the computer printout sheet. The calculations were carried out for $\theta = 57°$, $57°30'$, and $58°$, and by normalizing the printout to the trace from the spectrograph, direct comparisons can be made. These results are shown in Fig. 4(a), (b), and (c) where the dots are traced from the 704 printout and the line is traced from the spectrograph trace as in Fig. 3(c).

We pick the best value for the angle between the principal inertial axis system in $C_3H_4Cl_2^{35}$ and the principal quadrupole-coupling constant axis system of Cl^{35} as $57°30' \pm 15'$. Using this angle the value of χ_{ab} is calculated to be -51.5 ± 0.3 Mc. The principal quadrupole-coupling constants were also calculated and are $\chi_\alpha = -76.4 \pm 0.3$, $\chi_\beta = 37.0 \pm 0.3$, and $\chi_\gamma = 39.445 \pm 0.005$ Mc.

DIPOLE MOMENT

The Stark effect in the presence of quadrupole interaction can be calculated by straightforward but tedious means. However, by properly selecting components as well as exploiting the molecular symmetry, considerable simplification occurs. The matrix elements for the combined Stark and quadrupole interaction in the $(I_1 I_2 I J_\tau F M_F)$ representation are given by

$$\begin{aligned}&\langle I_1 I_2 I' J'_{\tau'} F' M_F \,|\, H_S + H_{Q_1} + H_{Q_2} \,|\, I_1 I_2 I J_\tau F M_F \rangle \\ &\quad = -E \sum_g \mu_g \alpha_{zg}(J'\tau', J\tau) \langle I J' F' M_F \,|\, \alpha \,|\, I J F M_F \rangle \qquad (8) \\ &\quad + f(I_1 I_2 I' J' F)[eQ_1 \langle \partial^2 V/\partial z^2 \rangle_1 + (-1)^{I'-I} eQ_2 \langle \partial^2 V/\partial z^2 \rangle_2],\end{aligned}$$

where H_S is the Stark perturbation, E is the external electric field, and μ_g (where $g = a, b, c$) are the dipole components of the molecule.

$$\alpha_{zg}(J'\tau', J\tau) = U^{-1} \alpha_{J'J} \alpha_{J'K',JK} U,$$

where $\alpha_{J',J}$ and $\alpha_{J'K',JK}$ are the usual direction cosines, and U is the transformation which diagonalizes the pure rotational Hamiltonian. The quadrupole part of this expression has been defined previously [see Eq. (2)] and the expansion of $\langle \partial^2 V/\partial z^2 \rangle$ is found in Eq. (3).

As there are only $\Delta M_F = 0$ interactions in Eq. (8), we can factor our matrices into blocks, each of which corresponds to a particular value of M_F. The rows and columns of each block are labeled by $J_\tau F I$. In 1,1-dichlorocyclopropane, the only nonvanishing component of the dipole moment is μ_b, leading to $A \leftrightarrow B_b$ and $B_a \leftrightarrow B_c$-type interactions. As was shown in the quadrupole interaction section, matrix elements involving the quadrupole part of Eq. (8) exist only for levels of like symmetry and $B_a \leftrightarrow B_b$, $A \leftrightarrow B_c$. Therefore, there are no common interactions between the Stark and quadrupole parts of Eq. (8). We can then arrange our matrices so that all quadrupole interactions are contained in submatrices along the diagonal (each submatrix labeled by J_τ and each matrix element in the submatrix by F and I). Since there are no common interactions, the Stark interactions will always appear in the off-diagonal submatrices.

The Stark interaction matrix elements in the $(IJFM_F)$ representation can be expressed in terms of the known matrices in the $(IM_I JK_J)$ representation by the following:

$$\langle I J' F' M_F \,|\, \alpha \,|\, I J F M_F \rangle = \sum_{M_I, M_J} \langle I J' F M_F \,|\, I J' M_I M_J \rangle \times \langle I J' M_I M_J \,|\, \alpha \,|\, I J M_I M_J \rangle \langle I J M_I M_J \,|\, I J F M_F \rangle. \qquad (9)$$

After evaluation of all the matrix elements, the diagonal block quadrupole submatrices can be diagonalized and the off-diagonal block dipole dependent submatrices transformed to this representation. Second order perturbation theory may then be applied to the coefficients in the off-diagonal blocks. The

$$\langle I J' F M_F \,|\, I J M_I M_J \rangle$$

transformation coefficients in Eq. (9) can be obtained from Condon and Shortley,[12] and Falk *et al.*[13] The transformed $\alpha_{zb}(J'\tau', J\tau)$ were computed on the IBM 704 electronic computer.

The transition studied was

$$1_{01}(F=4, I=3) \rightarrow 2_{12}(F=5, I=3).$$

Nuclear spin statistics make this transition the strongest of the $1_{01}-2_{12}$ multiplet. Using second order perturbation theory, the contribution to the energy for the $1_{01}(F=4, I=3, M_F=4)$ level is $-1.3762 \times 10^{-2} E^2 \mu^2$ Mc and for the $2_{12}(F=5, I=3, M_F=4)$ level is $-0.1788 \times 10^{-2} E^2 \mu^2$ Mc.

Experimentally, the Stark splitting was measured using the phase-stabilization system. The Stark modulation voltage consisted of a modified square wave. The bottom was flat and based on an accurately known bias voltage, and the top had an exponential shape as described previously. This enabled a presentation of the desired Stark components at the bias voltage, while at the same time the spectrum was cleared of the higher field components. Measurements were made by allowing the stabilized sweep to run continuously in one direction, while the bias voltage was being measured on a type K potentiometer with a calibrated voltage divider. After the frequency has passed the desired Stark component, the bias voltage was increased so that the Stark component was moved ahead of the klystron frequency and the process was repeated. The Stark splitting $\Delta\nu$ was found to be linear in the square of the electric field up to a $\Delta\nu$ of 2.60 Mc. Interference from

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[12] E. V. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), p. 277.

[13] D. L. Falk, G. S. Colladay, and R. E. Sells, Can. J. Phys. **30**, 253 (1952).

other components precludes measurements at greater splitting. The Stark coefficient, $\Delta\nu/E^2$, was found to be 3.00×10^{-2} Mc cm^2/v^2. These data yielded a dipole moment of 1.58M0.02 debye.

The linearity of the Stark effect versus the square of the field argues strongly for the validity of the use of second order perturbation theory. However, the Stark perturbation involves mixing between the 1_{01} and the 2_{12} levels. This in turn introduces off-diagonal terms in the previously diagonalized quadrupole submatrices. These elements connect levels which are very close together and may result in drastic errors. To avoid these, the complete matrices have been diagonalized using Stark perturbation elements calculated at several values of the field and using the above dipole moment. The second order perturbation theory was found to be valid over the range of our experimental measurements.

CONCLUSION

By comparison of the structure determination (Table IV) with the quadrupole section, the orientation of the quadrupole-coupling constant tensor with respect to the C—Cl internuclear line is obtained. The results show that the maximum electron density does indeed lie along the internuclear direction within the experimental error of 15 min of arc. Thus, it may be concluded that the C—Cl bonds are not bent in 1,1-dichlorocyclopropane.

The results show further that the electron distribution along the bond is not axially symmetric. The asymmetry is not large, however, with the greater electron density being perpendicular to the Cl—C—Cl plane. This asymmetry could be due to either Cl—Cl interaction or interaction of the C—Cl bond with the cyclopropane ring. Considering the Cl—Cl interaction, it is likely that the predominant contribution is due to the influence of the electric charge around one nucleus contributing to the gradient of the field at the other nucleus. Even when the Sternheimer[14] effect was considered, this effect was too small to explain the observed asymmetry. The asymmetry of this bond then may be taken as good evidence of π bonding between the chlorines and the ring. This bonding may take place through both the Cl$2p_\beta$[15] and Cl$2p_\gamma$[15] lone pairs, with the greatest loss coming from the Cl$2p_\beta$ orbital. This π bonding is further emphasized by the shortening of the C—Cl bond (1.73 A as compared to 1.77 in CH_2Cl_2).

No detailed explanation of the structure will be attempted in this paper, but there are several interesting aspects to the structure of 1,1-dichlorocyclopropane. The C—C bond length, 1.53 A, is much longer than the C—C bonds in ethylene oxide,[16] ethylene sulfide,[16] and cyclopropene.[17] Also, the three-membered ring is equilateral, but the H—C—H angle (117°35′) is appreciably larger than the Cl—C—Cl angle (114°38′).

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[14] R. M. Sternheimer, Phys. Rev. **94**, 1410A (1954).

[15] β and γ refer to the axes of the quadrupole tensor. Both β and γ are perpendicular to the C—Cl bond. β lies in the Cl—C—Cl plane, and γ lies perpendicular to the Cl—C—Cl plane.

[16] G. L. Cunningham, Jr., A. W. Boyd, R. J. Myers, and W. D. Gwinn, J. Chem. Phys. **19**, 676 (1951).

[17] P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, J. Chem. Phys. **30**, 512 (1959).